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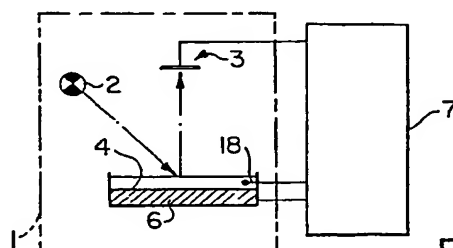
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54 Method & apparatus for monitoring cloud point or like transition temperatures.

57 Apparatus for monitoring the cloud point of a liquid, or the temperature at which any light scattering phase occurs therein, comprising a light-proof and light-absorbing chamber, and a liquid sample-receiving receptacle within the chamber having a bottom formed by a non-light-scattering surface; this surface being in thermal contact with a heating or cooling device, such as a thermoelectric cooler, and with a temperature measurement device. The chamber allows access to the receptacle so that sample liquid can be placed therein. A light beam source is located to direct a beam of light onto the surface at an incident angle so that light from the beam is reflected or absorbed by the surface. A light detector is arranged so as to detect scattered light which is produced when solid material forms in the liquid as it is cooled or disappears on heating. The melting point of a solid, or the boiling point of a liquid, can be detected, in addition to cloud points.



**FIG.1**

## Description

### FIELD OF INVENTION

This invention relates primarily to the measurement of the cloud point of petroleum oils. It may also apply to the measurement of the temperature at which a transition occurs between any transparent or translucent liquid and a light scattering phase, such as the formation of a solid, immiscible liquid, or gas phase in a liquid, and includes measurement of the melting point of a solid.

### BACKGROUND

The cloud point of petroleum oil, as defined by the American Society of Testing and Materials (ASTM) standard method D-2500, is the temperature at which haziness is first observed in a sample of oil which is cooled under prescribed conditions. The method requires that the sample be cooled in a series of constant temperature baths until the cloud point appears. The temperature of each bath, and the temperature at which the sample is transferred from one bath to the next one of lower temperature, are specified in the method.

The cooling rate of an oil sample treated in the manner described above is cyclical. The rate is highest after the sample is transferred due to the large difference in the temperature between the bath and the oil sample. From then on the cooling rate decreases as a function of time until the next transfer takes place. These different cooling rates give rise to inaccuracies of measurement; the true cloud point should be obtained under slow cooling, as it simulates the conditions for wax formation in equilibrium with the liquid phase. The preferred cooling rate for petroleum oils is one degree Centigrade per minute, or less. At cooling rates higher than this value the observed cloud point has a tendency to increase with increasing cooling rate and the precision of measurement deteriorates.

In addition, the current ASTM cloud point method requires a considerable amount of an operator's time to make one determination. An operator's subjective judgement is also required to determine the onset of haziness in the sample.

Since the cloud point method has been established, numerous inventors have come forward with ideas to automate the measurement. Most of the ideas were centred around improvements related to the automatic detection of cloud formation and automatic charging and discharging of a sample cell. These systems tend to be expensive and have various drawbacks.

Thus, many prior art systems require complex and expensive cooling systems either because a large sample of liquid is required or because a fairly large chamber is cooled. Use of a large sample also gives rise to possible inaccuracies caused by lack of temperature uniformity. Such systems are described in :-

- 5 U.S. Patent No. 3,077,764 which issued Feb. 19, 1963 to Kapff;
- U.S. Patent No. 3,248,928 which issued May 3, 1966 to Conklin et al.;
- U.S. Patent No. 3,527,082 which issued Sept. 8, 1970 to Pruvot et al.;
- 10 U.S. Patent No. 3,580,047 which issued May 25, 1971 to Simpson;
- U.S. Patent No. 3,643,492 which issued Feb. 22, 1972 to Simpson;
- 15 U.S. Patent No. 3,447,358 which issued June 3, 1969 to Crespin et al.; and
- U.K. Patent No. 1,438,754 published June 9, 1976.

Other prior art systems have generally enclosed cells or containers through which the liquid sample is caused to flow. In addition to being relatively complicated, such arrangements may make cleaning of the cell or vessel difficult. Such arrangements are shown in:-

- 20 U.S. Patent No. 3,187,557 which issued June 8, 1965 to Holbourne
- 25 U.S. Patent No. 3,457,772 which issued July 29, 1969 to Chassagne et al.
- U.S. Patent No. 3,545,254 which issued Feb. 13, 1968 to Chassagne et al.
- 30 U.S. Patent No. 4,519,717 which issued May 28, 1985 to Jones et al.

U.S. Patent No. 3,807,865 (issued April 30, 1974 to Gordon et al.) shows an arrangement in which a small sample of liquid is placed in a glass tube which has previously been sealed at one end, and which is then "drawn off and sealed as close to the upper meniscus of the sample as convenient". The tube is placed in a flowing heat transfer fluid to effect cooling; temperature is measured by a thermometer close to the tube. The presence of a solid phase is detected by monitoring for light scattered when a light beam is passed axially into the tube.

In most of the proposals described in previous patents, the cooling rate of the oil sample was either poorly defined or uncontrolled. For example, U.S. Patent No. 3,187,557 suggests a quick cooling as it mentions a 60 times decrease in analysis time as compared with the ASTM method. In U.S. Patent No. 4,519,717, a variable cooling rate is suggested and the analysis time is several times shorter than the ASTM method. Such high cooling rates have been shown to result in inaccuracy.

### SUMMARY OF THE INVENTION

The invention provides both a method and apparatus primarily intended for the measurement of cloud point, but also suitable for measuring the temperature at which any light scattering phase forms or disappears in a transparent liquid when this is heated or cooled. Such phase may be a solid, an immiscible liquid or a gas. Thus, the invention can be

used for measuring the temperature of transitions between miscible and immiscible liquids, of production of a gaseous phase when a liquid boils, and transitions between a solid and liquid at melting or solidification.

In accordance with one aspect of the present invention, a method for the measurement of the temperature at which a transition occurs between a transparent or translucent liquid and a light scattering phase comprises:

- placing a sample of the liquid in a shallow receptacle having a bottom formed of heat conductive material in thermal contact with temperature changing means and temperature measurement means, said bottom having an upper surface which is non-light scattering (ie. highly reflective or light-absorbing),
- shining a light beam towards said upper surface at an incident angle thereto such that, in the absence of said light scattering phase, the light passes through said sample and is either largely absorbed by said surface, or is reflected by the surface along a reflected light beam path,
- monitoring the intensity of light from said beam scattered from the said sample,
- warming or cooling said surface by said temperature changing means while said light beam is continued to be shone onto said surface and the intensity of the light scattered from the sample is continued to be monitored,
- detecting a change in intensity of the scattered light and determining the temperature of said surface when such change in intensity occurs.

According to another aspect of the invention, apparatus for measuring the temperature at which a transition occurs between a transparent or translucent liquid and a light scattering phase, comprises:

- a generally light proof chamber having light-absorbing internal surfaces;
- a liquid sample-receiving receptacle within said chamber and having its bottom formed by a heat conductive material with an upper surface which is non-light scattering;
- means allowing access to the chamber for placing a sample of liquid in said receptacle and allowing removal of the liquid from the receptacle at the termination of the test;
- means in thermal contact with said bottom for changing the temperature of said surface and means for determining the temperature of said surface in thermal contact therewith,
- a light beam source located to direct a beam of light onto said surface at an incident angle so that light from the beam is largely reflected or absorbed by said surface, and
- scattered light detection means arranged so as to detect light scattered by said sample and changes in intensity of the scattered light and connected into circuit means capable of registering a change in light scattered from the said sample as said surface is heated or cooled.

In this invention, the receptacle can be quite small and will be shallow, ie. having a depth much less than the width or length. This means that only a small quantity of sample (a few drops) is required, and the

receptacle is easily cleaned. The receptacle may be open-topped or have a transparent cover.

The said surface is preferably a smooth horizontal mirror surface. In this case the scattered light is of course measured at a location sufficiently separated from the light beam reflected from the mirror surface so that the reflected beam does not interfere with scattered light measurements. Preferably, the incident angle between the light beam and the surface is an acute angle of from  $20^\circ$  to  $80^\circ$ , and the scattered light is measured in a direction perpendicular to the surface.

The invention will be described in more detail with reference to the accompanying drawings, which show a preferred embodiment of the apparatus, and in which:-

Figure 1 is a schematic diagram of the apparatus including associated electrical components;

Figure 2 is a sectional elevation through the apparatus; and

Figure 3 is a detailed sectional view of the light detector.

Figs. 4 to 11 are graphs showing the changes of scattered light intensity with changes in temperature, obtained using the method and apparatus of this invention, for the following phase changes:

Figure 4: solid - liquid system: cloud point for diesel oil;

Figure 5: solid - liquid system: freezing point of distilled water;

Figure 6: solid - liquid system: freezing point of cyclohexane;

Figure 7: solid - liquid system: freezing point of benzene;

Figure 8: solid - liquid system: freezing point of sodium chloride solution;

Figure 9: solid - liquid system: freezing point of 30% antifreeze, 70% water mixture;

Figure 10: immiscible liquids: 30% triethylamine, 70% water; and

Figure 11: liquid - gas system: boiling point of N-butane.

The cloud point measurement device shown in Figures 1 and 2 consists of a light proof chamber 1, a light source 2, a light detection unit 3, a non-light scattering surface 4 which forms the bottom of a receptacle for a liquid sample, a thermoelectric cooler 6 in thermal contact with the surface 4, and a data acquisition unit and control unit 7 for the device. The thermoelectric cooler can be used both for cooling and for heating.

The chamber 1 is designed to withstand low gas pressure of approximately 5 - 10 psig., and two gas inlet/outlet ports 11 and 12 located in the lower portion of the chamber allow the chamber to be purged with a dry gas to avoid condensation of water inside the unit. The chamber has a removable lid portion 1a, held in place by hinges (not shown) and by clamps 13 which engage peripheral flanges 14. The entire inner surface of chamber 1 and all the inner attachments, except for the surface 4, is light absorbing and preferably is black, to prevent reflection of light from these surfaces.

The light source 2 is a light-emitting diode mounted on a 1/8" (3mm) rod 16 which can be moved in the vertical direction and can also be rotated to allow the best adjustment of incidence angle of the light beam on the surface 4. The angle of incidence between the light beam and the surface 4 is always an acute angle within the range from 20° to 80° and preferably about 45°.

The non-light scattering surface is located at the centre of the cell. In this preferred embodiment, this is a highly polished flat mirror forming the top surface of the bottom of a receptacle for the sample. As shown, this is an open topped receptacle having an annular sidewall 17, both the bottom and sidewall being formed integrally of copper. The receptacle is shallow in relation to its width being about 2mm deep so as to contain a maximum of 0.2 cc of liquid.

The mirror 4 is mounted on the top surface of thermoelectric cooler 6 so as to be in good thermal contact therewith, and the temperature of the surface is measured by a platinum resistance thermometer 18 affixed to the bottom part of the mirror and also in good thermal contact therewith. Other suitable temperature measurement devices may be used. The cooler 6 is capable of removing heat from the mirror and delivering it to a heat sink 19.

The light detection unit 3, used to detect scattered light produced at the formation of a light scattering phase, is placed directly above the mirror 4 so as to be on a light transmittance path perpendicular to the mirror. This unit, shown in Fig. 3, consists of a charge coupled device (CCD) 20 for detecting the intensity of scattered light, and a convex lens 22 held by O-ring 23 to focus the light onto the detector. The CCD is mounted on a plastic rod 24, movable in the vertical direction. This allows the best adjustment of the CCD for reception of the scattered light through the fixed lens.

The data acquisition and control unit 7 is used to collect information from the thermocouple 18 and the CCD 20, to control the cooling rate of the mirror 4 and also to determine the transition temperature such as onset of cloud point. A computer equipped with the necessary software and hardware is utilized for this purpose.

The method of operation, when used for detecting cloud point in a liquid, will now be described with reference to Fig 4, which shows results obtained in testing a Diesel oil is as follows:

Prior to the test, one must ensure that the mirror 4 is clean and dry. The lid portion 1a of the chamber is opened, and liquid sample is introduced into the chamber by using a pipette or dropper to place about 0.1-0.2 mls of liquid onto the mirror 4, followed by closing and clamping the lid. The chamber is then purged slowly with a dried gas for about two minutes and then kept pressurized at a level of 1-2 psi. The temperature of the mirror is lowered by cooler 6 at a predetermined rate, about 0.8 °C/min., the light source 2 is activated and the light beam is directed onto the mirror 4. Prior to the formation of cloud in the sample, the light beam is almost entirely reflected, and only a small amount of scattered light is detected by the detection unit 3;

this is shown as a generally horizontal line in Fig 4. Once clouds or wax crystals start to form, the intensity of scattered light increases; Fig 4 shows that this occurs between -27.5°C and -28°C. Therefore, by monitoring the light intensity received by the detector unit 3 as a function of temperature, the cloud point of the sample can be determined. At the end of the test, the thermoelectric cooler is switched off to allow the temperature of the mirror to return to ambient. The unit is then depressurized and opened up to allow cleaning of the sample receptacle.

As compared to prior art mechanized systems, the present invention has the following advantages:

1. It requires only a very small amount of liquid sample; in the embodiment described this is less than 0.2 cc. A greater depth might be used but this is expected to be less than 1.0 cm and preferably less than 5mm.

2. The small amount of cooling capacity required means that a relatively cheap thermoelectric cooler can be used in place of much more expensive conventional refrigeration apparatus. In some instances, such devices may also be used to heat the sample above ambient temperature.

3. The shallow receptacle is easily cleaned, preventing cross-contamination.

4. Any lack of uniformity of temperature from top to bottom of the sample does not seriously affect the results. In the cooling mode the bottom of the sample will be coldest, but as soon as any cloud or crystals occur at this point the CCD will register scattered light; the presence of warmer liquid towards the top of the receptacle is of no consequence. Since the temperature measuring device is in thermal contact with the bottom of the receptacle this accurately measures the temperature at which the cloud point occurs.

While a highly polished mirror has been found to give the best results, useful measurements can also be made using a receptacle the bottom surface of which is black and therefore light absorbing, and substantially non light-scattering. Both smooth and rough black surfaces can be used.

The apparatus has been described as using an open-topped receptacle, which is of course the most convenient. However, a receptacle with a transparent lid may be used for volatile liquids and to prevent drying during an experimental run.

Figs. 5 to 12 show graphs of other experiments done with various systems.

Figure 5 summarizes the results of an experiment with distilled water. The experiment started at point "A" where the liquid was cooled down slowly. The light scattering intensity did not increase as the temperature passed 0°C due to supercooling of the liquid. Finally, nucleation of ice occurred at point "B", followed by a rapid crystal growth period and simultaneous release of latent heat. The fast rise of latent heat caused the temperature of the system to rise to point "C".

Beyond point "C", the growth of crystals slowed down gradually until the entire sample was solidified

at point "D". At that stage, the cooling power of the cooler was reduced and the temperature of the system was allowed to rise. At point "E", where the temperature was 0°C, the scattered light intensity dropped as the melting process began. The sample was close to completely melted at point "F".

Figures 6 and 7 show the results for other pure liquids, respectively cyclohexane and benzene. The melting points determined by the device agreed well with those reported in the literature as shown on the graphs. In Figure 6, the latent heat effect was not apparent mainly because the latent heat of solidification of cyclohexane is very low (approximately 1/13 of that corresponding to water). It may be noted that due to supercooling effects it is usually only the melting point, and not the solidification point, which can be compared with literature values.

Figure 8 shows the results for a 60% sodium chloride and water mixture. It can be seen that the melting point compares very well with the literature value.

Figure 9 shows the results for an ethylene glycol-water system. The freezing and melting temperatures were distinctly measured even though the mixtures were translucent rather than transparent. The measured values for melting point compared well with the literature value.

The detection of an immiscible liquid phase is shown in Figure 10. This is a system with 30% triethylamine and 70% water. According to the literature, the system is completely miscible at temperatures below about 18.5°C and becomes immiscible at temperatures higher than this level.

The experiment began at about 15°C and the system was warmed up gradually. At about 18.1°C, the scattered light intensity increased significantly due to the separation of the two liquid phases. When the two phase system was cooled from 20°C, the two liquid phases became completely miscible again at about 18.1°C.

The results for a liquid-gas system are shown in Figure 11. This shows the ability of this device to detect the boiling point of normal butane. The experiment began at about -11°C, which was well below the boiling point of n-butane. As the temperature of the sample increased to -3.7°C, the scattered light intensity rose substantially and then went up and down depending on the number and size of bubbles in the liquid phase. This behaviour continued until the entire sample was boiled off. It should be noted that in this experiment, the measurement cell was completely air-free; the vapour space of the cell was occupied by n-butane vapour.

## Claims

1. A method for the measurement of the temperature at which a transition occurs in a material between a transparent or translucent liquid phase and a light scattering phase, which method comprises:

- placing a sample of the material in a receptacle;
- shining a light beam onto the sample such

that, in the absence of said light scattering phase, the light passes through said sample without substantial scattering;

- monitoring the intensity of light from said beam scattered from the said sample while changing the temperature of the sample by temperature changing means while said light beam is continued to be shone onto said sample;

- detecting a change in intensity of the scattered light and determining the temperature of said sample when such change in intensity occurs; and

- characterized in that said receptacle is shallow and has a bottom formed of heat conductive material in thermal contact with said temperature changing means and also with temperature measurement means, said bottom having an upper surface which is non-light-scattering and which is such that, in the absence of a light scattering phase, the light of said beam is either largely absorbed by the surface or is reflected along a light beam path.

2. The method of claim 1 wherein surface is a flat mirror surface, the incident angle between the light beam and said upper surface being an acute angle of from 20° to 80°, and wherein the light scattered from said sample in a direction generally perpendicular to the surface is detected.

3. A method according to claim 1, wherein the depth of the liquid sample is less than 1cm.

4. A method according to claim 1, wherein said temperature changing means is a thermoelectric device.

5. A method according to claim 1, wherein the receptacle is a shallow receptacle having an open top, with said surface providing a substantially flat bottom.

6. A method according to claim 1, wherein the liquid is volatile and wherein the receptacle has a transparent top which is removable to allow for cleaning.

7. Apparatus for measuring the temperature at which a transition occurs between a transparent or translucent liquid and a light scattering phase, comprising:

- a chamber;
- a liquid sample-receiving receptacle within said chamber;
- means allowing for placing a sample of liquid in said receptacle and allowing removal of the sample at the termination of the test;
- means for changing the temperature of said sample and means for indicating the temperature of said sample;
- a light beam source located to direct a beam of light into said sample;
- scattered light detection means arranged so as to detect light scattered by said sample and changes in intensity of the scattered light;
- characterized in that said chamber is a generally light proof chamber (1) having light-absorbing internal surfaces, in that said receptacle (4, 17) has a bottom (4) formed by a heat

conductive material having an upper surface which is non-light scattering, said bottom being in thermal contact with the means for changing temperature (6) and the means for indicating temperature (18), and in that the light beam source (2) is located to direct said beam at an incident angle to said upper surface so that light from the beam is largely reflected or absorbed by said upper surface.

8. Apparatus according to claim 7 including a data processing and control means (7) to control changing the temperature of the said surface.

9. Apparatus according to claim 7 wherein said surface (4) is a flat mirror surface, said incident angle between the light beam and said surface is an acute angle of from 20° to 80°, and said scattered light detection means (20) is located along a light transmittance path generally perpendicular to said surface.

10. Apparatus according to claim 7, wherein the receptacle is a shallow receptacle having an open top, with said surface (4) providing a

substantially flat bottom.

11. Apparatus according to claim 7, wherein the receptacle has a transparent top which is removable for cleaning.

12. Apparatus according to claim 7, wherein said receptacle has a depth small in proportion to its width.

13. Apparatus according to claim 7, wherein said means for changing temperature is a thermoelectric cooler (6) in contact with said surface.

14. Apparatus according to claim 7, wherein said chamber has an inlet (11) and an outlet (12) for a drying gas.

15. Apparatus according to claim 7, wherein said means for determining the temperature of the surface is an electrical heat sensitive device (18) in direct contact with said surface.

16. Apparatus according to claim 7, wherein the bottom of said receptacle is formed integrally of a heat conductive metal.

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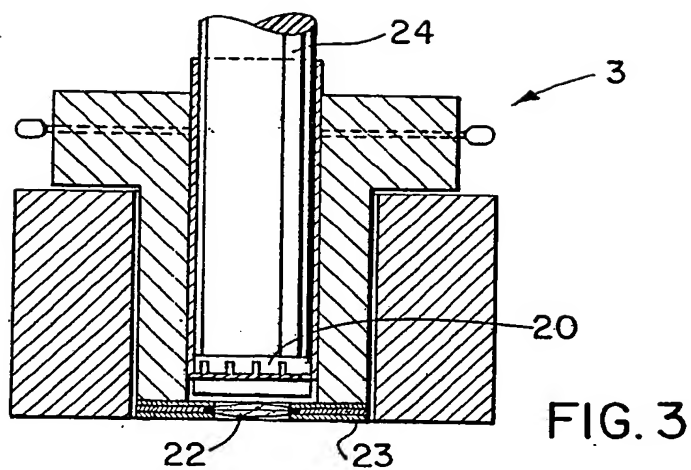
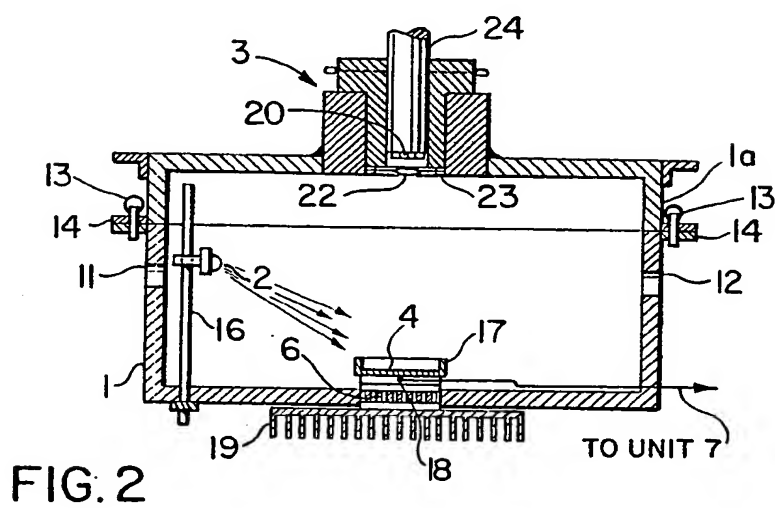
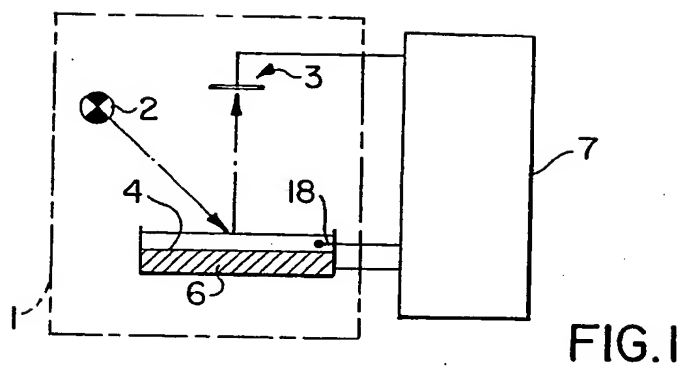
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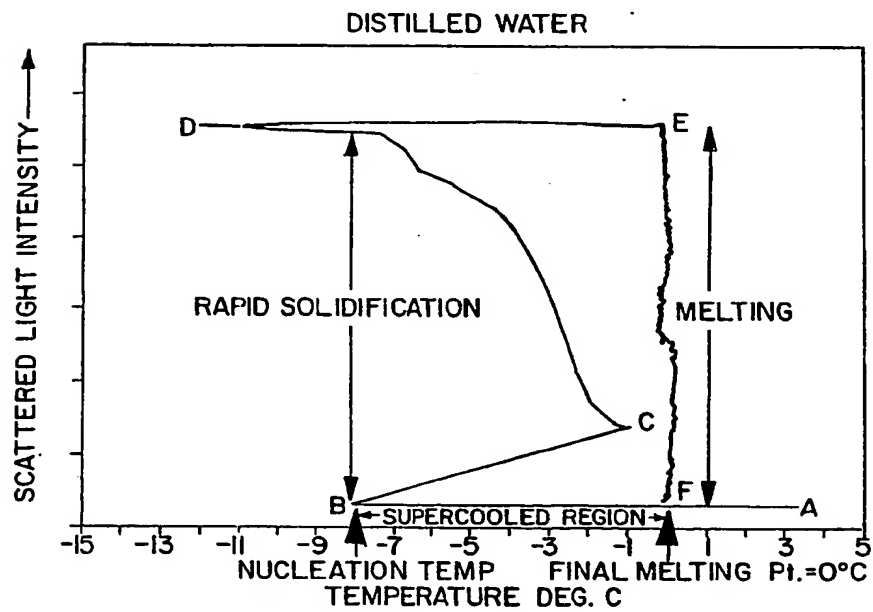
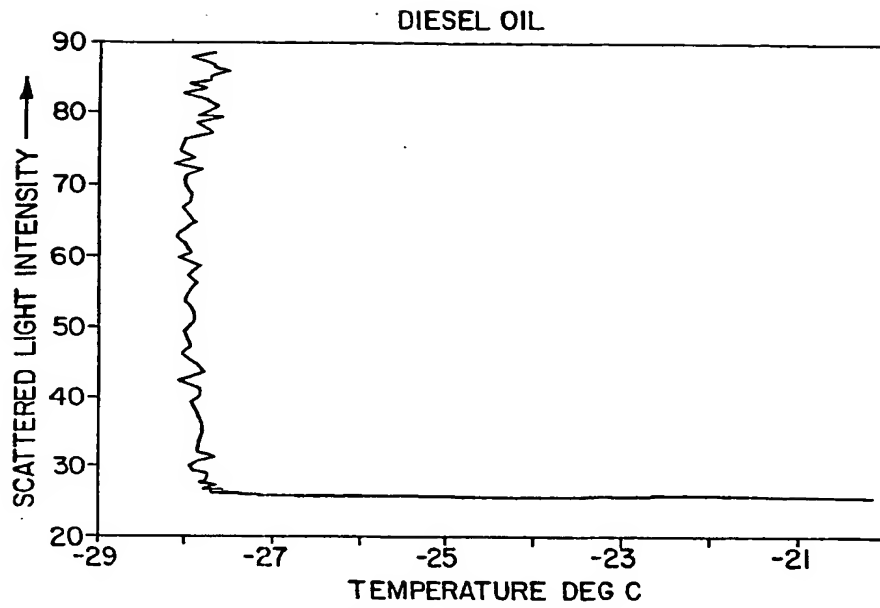
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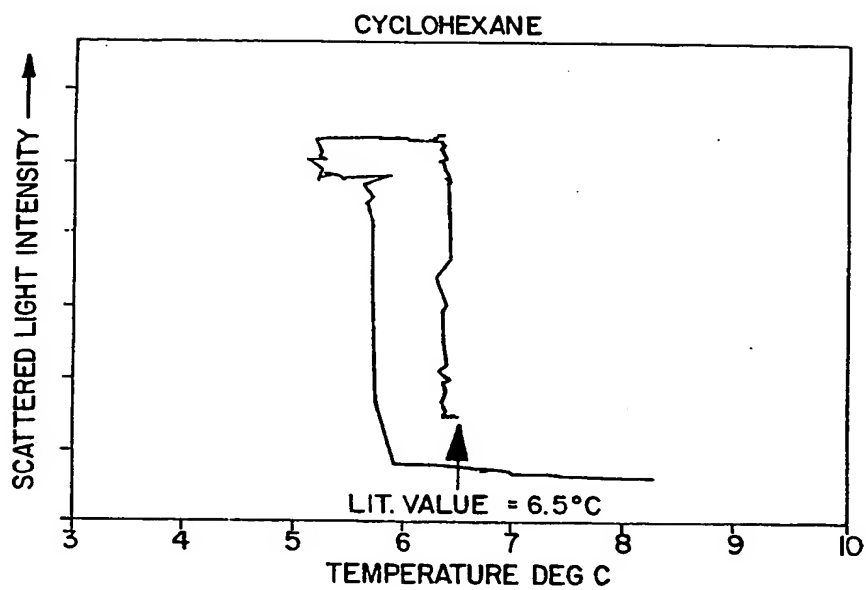


FIG. 6

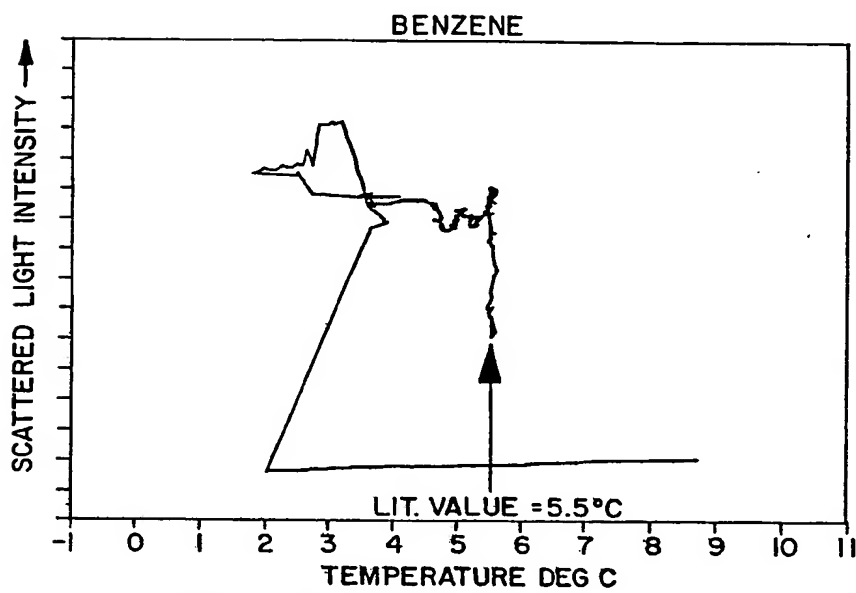


FIG. 7

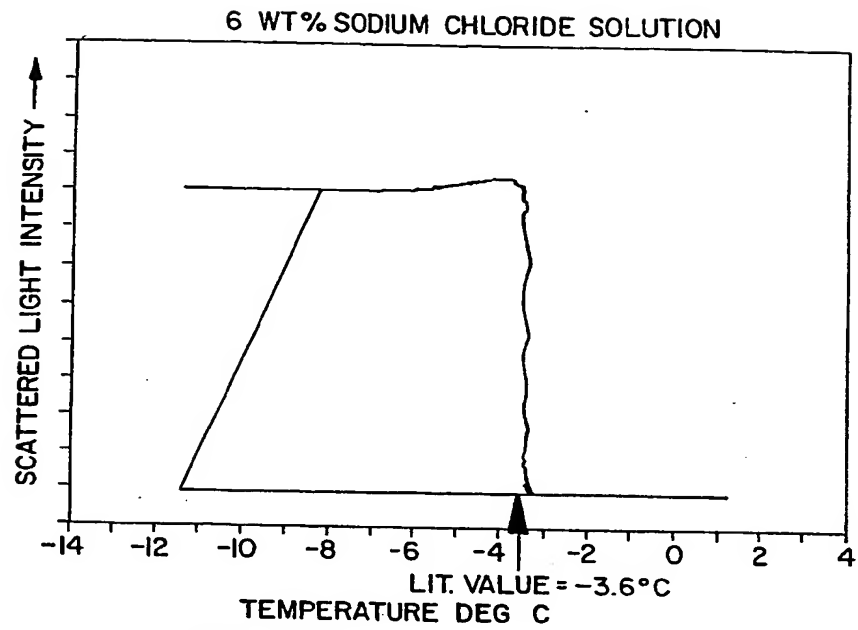


FIG. 8

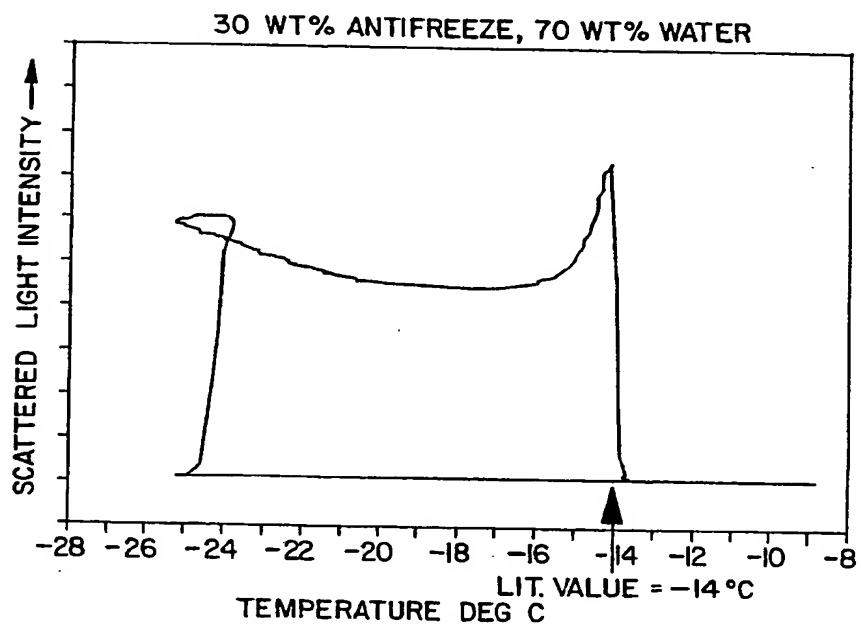


FIG. 9

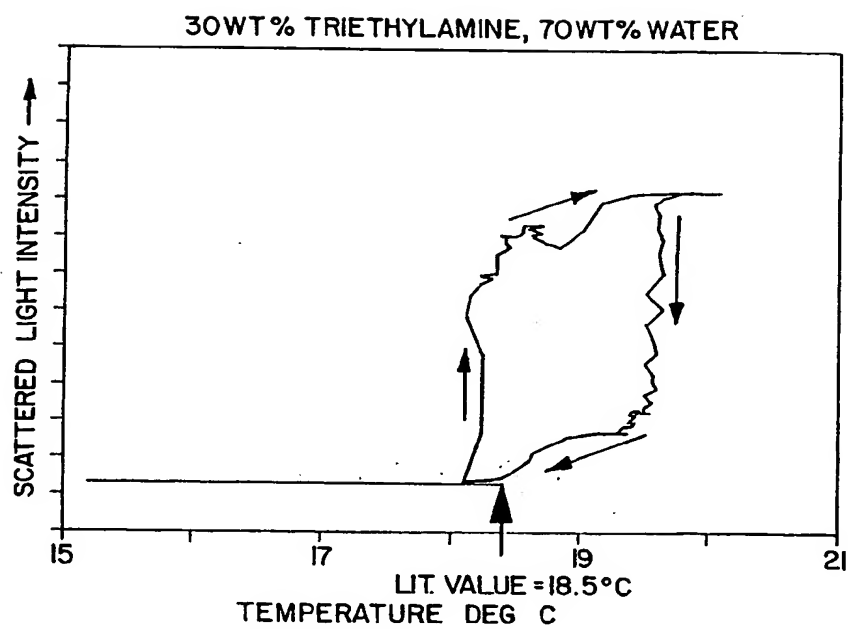


FIG. 10

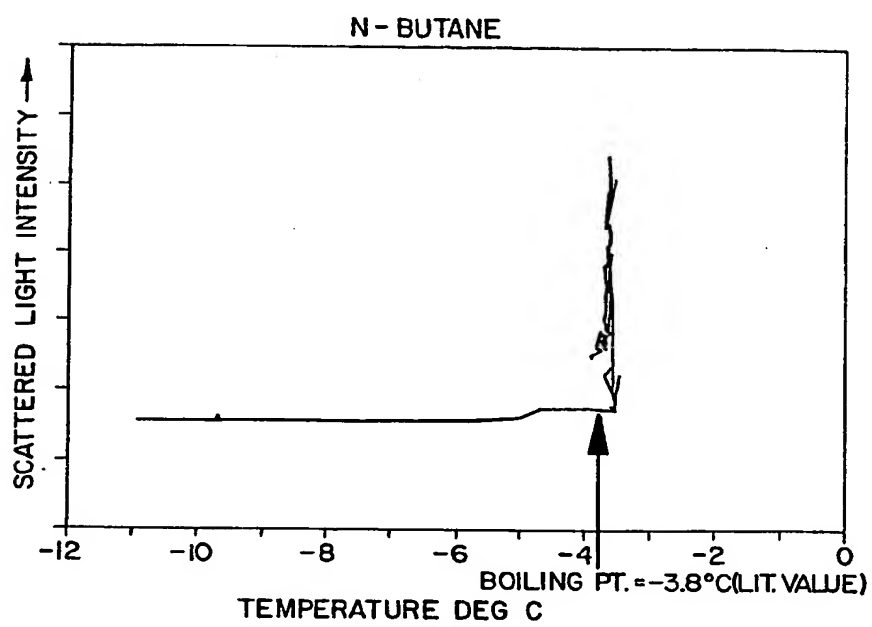


FIG. 11

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54 Method & apparatus for monitoring cloud point or like transition temperatures.

57 Apparatus for monitoring the cloud point of a liquid, or the temperature at which any light scattering phase occurs therein, comprising a light-proof and light-absorbing chamber, and a liquid sample-receiving receptacle within the chamber having a bottom formed by a non-light-scattering surface; this surface being in thermal contact with a heating or cooling device, such as a thermoelectric cooler, and with a temperature measurement device. The chamber allows access to the receptacle so that sample

liquid can be placed therein. A light beam source is located to direct a beam of light onto the surface at an incident angle so that light from the beam is reflected or absorbed by the surface. A light detector is arranged so as to detect scattered light which is produced when solid material forms in the liquid as it is cooled or disappears on heating. The melting point of a solid, or the boiling point of a liquid, can be detected, in addition to cloud points.

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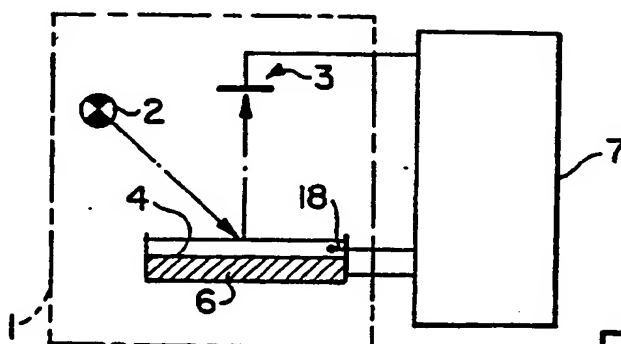


FIG.1



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 89 30 1141

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A,D	US-A-4 519 717 (JONES et al.) * Front page *	1	G 01 N 33/28 G 01 N 25/04
A,D	US-A-3 187 557 (HOLBOURNE et al.) * Whole document *	1	
A,D	GB-A- 966 828 (STANDARD OIL CO.) * Whole document *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			G 01 N
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31-05-1990	Examiner KOUZELIS D.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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